

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08L 101/00 // (C08L 101/00 C08L 67:02) , 67/02	A1	(11) International Publication Number: WO 92/13921 (43) International Publication Date: 20 August 1992 (20.08.92)
(21) International Application Number: PCT/US92/01003 (22) International Filing Date: 6 February 1992 (06.02.92) (30) Priority data: 652,809 8 February 1991 (08.02.91) US (71) Applicant: EASTMAN KODAK COMPANY [US/US]; 343 State Street, Rochester, NY 14650-2201 (US). (72) Inventors: KRUTAK, James, John, Sr. ; 6305 Booth Court, Kingsport, TN 37663 (US). WEAVER, Max, Allen ; 125 Hill Road, Kingsport, TN 37664 (US). PARHAM, William, Whitfield ; 1917 Hermitage Drive, Kingsport, TN 37664 (US). POLLOCK, Mark, Alan ; 201 East Eight Avenue, Johnson City, TN 37601 (US). BELL, William, Paul ; 182 Harmony Acres Drive, East, Jonesborough, TN 37659 (US). KEEGAN, Michael, James ; 525 Wake- field Court, Kingsport, TN 37663 (US).		(74) Agent: GRAVES, Bernard, J., Jr.; 343 State Street, Ro- chester, NY 14650-2201 (US). (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European pa- tent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (Euro- pean patent), IT (European patent), JP, KR, LU (Euro- pean patent), MC (European patent), NL (European pa- tent), SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: THERMOPLASTIC POLYMERS COLORED WITH POLYESTER COLOR CONCENTRATES**(57) Abstract**

Colored thermoplastic polymers comprising a blend of one or more thermoplastic polymers and colored polyesters are provided. Such colored thermoplastic polymers thus provided have uniformity and stability in color hue.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	MI	Mali
AU	Australia	FR	France	MN	Mongolia
BB	Barbados	GA	Gabon	MR	Mauritania
BE	Belgium	GB	United Kingdom	MW	Malawi
BF	Burkina Faso	GN	Guinea	NL	Netherlands
BG	Bulgaria	GR	Greece	NO	Norway
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IE	Ireland	RO	Romania
CA	Canada	IT	Italy	RU	Russian Federation
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroun	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark	MG	Madagascar		
ES	Spain				

- 1 -

**THERMOPLASTIC POLYMERS COLORED WITH
POLYESTER COLOR CONCENTRATES**

Field of the Invention

5 This invention belongs to the field of polymer chemistry. More particularly, this invention relates to thermoplastic polymers colored with colored polyesters.

Background of the Invention

10 It is well-known that thermoplastic polymers may be colored by adding pigments or solvent dyes (e.g., see Thomas G. Weber, Editor, Coloring of Plastics, John Wiley and Sons, New York, 1979). The use of pigments, however, is accompanied by undesirable
15 properties such as opacity, dullness of color, low tinctorial strength, etc. Also, difficulties in uniformly blending the insoluble pigments with the thermoplastic resin are encountered. Also useful for coloring thermoplastic polymers are solvent dyes
20 (K. Venkataraman, Editor, The Chemistry of Synthetic Dyes, Vol. 8, Academic Press, New York, 1978, pp 81-131), which give compositions having improved clarity, brightness in hue and high tinctorial strength, but which may lead to dye migration, extraction, etc.
25 from the colored thermoplastic resin. These problems are of particular concern when solvent dyes are used to color flexible polymers such as polyvinyl chloride, polyethylene and polypropylene which have low glass transition temperatures.

30 It is also known that one can prepare solvent soluble nonextractable polymeric aminotriarylmethane dyes having polyester, polycarbonate, polyurethane, or polyethyleneimine backbones and incorporate them into polymers such as polyvinyl chloride, polyvinylidene

- 2 -

chloride and acrylic polymers such as poly(methyl methacrylate) etc. by solvent blending techniques [U.S. Patent 4,477,635 (1984)]. Difficulties are encountered in preparing these polymeric colored compounds because a
5 non-colored intermediate aromatic amine containing polymer must be prepared and then the aromatic amine moiety in the polymer structure must be converted into an aminotriarylmethane moiety by further reaction with a diaryl ketone in the presence of a condensation
10 catalyst such as phosphorous oxychloride in an inert organic solvent. Attempts to make colored polyester compositions in one step by copolymerizing aminotriarylmethane colorants containing reactive groups generally fail, presumably because of the thermal instability of
15 the triarylmethane chromophore. These previously disclosed polymeric aminotriarylmethane compositions also have poor fastness to light and do not have the requisite thermal stability for use in coloring thermoplastic polymers via the more favorable method of
20 high temperature melt blending.

It is further known [U.S. Patent 4,116,923 (1978)] that one may color plastics, in particular polyolefins, with low melting, cross-linked colored polyester compositions containing residues of terephthalic acid,
25 isophthalic acid, or both, a low-molecular weight trimethylol alkane, i.e., 1,1,1-trimethylol propane and a copolymerizable colorant, said colorant being present at a level of 0.1-25% by weight. Difficulties are encountered, however, in preparing these highly cross-
30 linked colored polymers as extreme care with regard to the temperature, amount of vacuum, the level of colorant present and the reaction time is necessary to attempt to reproduce the same quality of cross-linked colored

- 3 -

polyester composition. Further, these colored polyester compositions are brittle and low melting and may cause deterioration in physical properties of thermoplastic resins when added in quantities sufficient to produce a high level of coloration. Critical in the preparation of these previously disclosed polymers is the achievement of a low degree of polymerization to give a low melting polymer which has adequate solubility characteristics in the polymer to be colored; however, to accomplish this the colorant may not be copolymerized, particularly when added at high levels, thus leading to undesirable extractable colorant.

Finally, it also is known to color thermoplastic polymeric materials using color concentrates consisting of physical admixtures of polymers and colorants. However, the use of such physical admixtures to color polymeric materials such as polyesters, e.g., poly-(ethylene terephthalate) and blends thereof, present a number of problems:

20

(1) Colorant migration during drying of the colored polymer pellets.

25

(2) Colorant migration during extrusion and colorant accumulation on dies which can cause film rupture and shut-downs for clean-up, etc. Such colorant migration and accumulation result in time consuming and difficult clean-up when a polymer of another color is subsequently processed in the same equipment.

30

- 4 -

(3) Colorants may not mix well, for example, when using two or more color concentrates to obtain a particular shade.

5 (4) Colorants may diffuse or exude during storage of the colored polymeric material.

Furthermore, the presence of oligomeric material in the polymers, such as polyester, admixed with the
10 colorants to produce the known color concentrates can cause problems of equipment contamination during processing.

As noted above, inorganic and low molecular weight organic compounds are widely used as colorants for
15 polymeric materials. By proper combination of colors, nearly any color can be generated. However, there are problems with this coloration system, including chemical incompatibility between the colorant and polymer and the carcinogenic and/or toxic nature of many of the
20 colorants. Of particular concern in the injection molding of polyesters and blends of polyester and polycarbonate is the appearance of a discolored, dark streak at weld lines. Weld lines are formed in an injection molded part whenever two advancing melt fronts
25 meet. This problem is particularly severe when dark reds and greens are desired. Because these discolored weld lines are unacceptable in aesthetic applications, these materials often cannot be used in large parts which require multiple gates.

30

- 5 -

Summary of the Invention

This invention relates to thermoplastic polymers such as polyesters, polyolefins, polycarbonates, cellulose esters, polyurethanes, polyamides, etc., having blended therein as colorant one or more polyester color concentrates having copolymerized therein from about 1 to about 50% by weight of one or more thermally stable copolymerizable colorants. The polyester color concentrates may be amorphous, partially crystalline or highly crystalline and exist in powder or pellet form. They may be incorporated into the thermoplastic polymers by conventional methods to produce plastic compositions useful for a variety of end uses where nonmigrating or nonextractable colorants are needed. The uniformity and stability of the colored thermoplastic polymers thus provide shaped or formed colored thermoplastic articles which are uniform in color and do not form highly visible weld lines which are typically found in thermoplastic polymers colored with traditional pigments.

Because these thermoplastic blends can be molded without visible weld lines, they are especially useful in the injection molding of large parts such as recreational and utility vehicle housing and automotive body panels.

Detailed Description of the Invention

This invention relates to thermoplastic polymer compositions having blended therewith as colorant one or more colored polyester compositions having copolymerized therein from about 1% to about 50% of one or more thermally stable copolymerizable colorants.

- 6 -

Such colorants thus will not extract, leach, migrate, exude or sublime during the high temperatures necessary for extrusion or molding of thermoplastic polymeric materials. There are serious toxicity concerns
5 regarding the use of organic pigments and soluble dyes to color thermoplastic materials since some of these colorants have been shown to be potential carcinogens or to cause contact dermatitis [Federal Register (July 15, 1988); *Plastics World* (October, 1990, pp 49-54); ACTA
10 Derm. Venerol., Suppl. 1987, 134, pp 95-97; S. Fregert, Manual of Contact Dermatitis, Munksgard, Denmark (2nd Ed. 1981)].

The overall purpose of this invention is to provide colored thermoplastic blends wherein the molecular
15 colorants will not be leachable, sublimable, extractable, or be removed by migration or exudation from the thermoplastic blends thus minimizing the toxicity concern relative to human exposure. Another purpose of the invention is to provide nonhazardous colored thermoplastic compositions having good brilliance, clarity and
20 fastness to sunlight, high heat stability, excellent homogeneity of colorant, and which normally maintain the desirable physical properties of the uncolored thermoplastic materials. Another purpose of the invention is
25 to provide colorant materials which can be blended with thermoplastic polymers and molded to provide thermoplastic blends without visible weld lines.

Accordingly, the present invention provides a thermoplastic polymer having admixed therein one or
30 more colored polyesters, said colored polyesters comprised of at least 1.0 weight percent of one or more thermally-stable, difunctional colorant compounds of Formula I copolymerized therein.

- 7 -

In general, such thermally-stable difunctional colorants may be represented by the formula



5 wherein "Col" is the residue of a thermally-stable organic colorant and X is a polyester reactive group, i.e., a group reactive with at least one of the monomers from which the polyester is prepared. In particular, 10 compounds of Formula (I) are those described in copending U.S. Application Serial No. 07/604,311, incorporated herein by reference.

The powder colorant compositions provided by U.S. Serial No. 07/604,311 comprise a semicrystalline 15 polyester, in a finely-divided form, having copolymerized therein at least 1, more typically at least 5, weight percent, based on the total weight of the compositions, of the residue of a thermally-stable, difunctional colorant compound. Since the powder 20 compositions have colorant residues incorporated into the polymer chain, the colorant is not leachable, sublimable or extractable and does not exude or migrate from the composition. The colorant compositions are in the form of a finely-divided, colored microcrystalline 25 polyester powder capable of being used in a wide variety of products such as cosmetics, skin creams or lotions, soaps, hair colorations, waxes, polishes, coatings, paints, toners for impactless printing, inks, etc., which will be safe to humans since exposure to toxic 30 molecules readily absorbed by the body is greatly minimized. Thus, the colorant compositions have utility in a wide variety of applications where toxicological concerns are evident. The concentrate materials may be

- 8 -

used for imparting color to a wide variety of thermo-plastic compositions including polyesters, poly-carbonates, polyamides, cellulose esters, polyurethanes, polyolefins, etc., by conventional melt or solution
5 blending techniques. When using the polymeric color concentrates of this invention, the colorant problems relative to toxicity concerns are largely overcome.

The powder colorant compositions thus provided may be obtained by means of a dissolution-crystallization-precipitation procedure wherein a polyester color
10 concentrate, preferably an amorphous or partially crystalline polyester color concentrate, is dissolved in an organic solvent from which the colorant composition is recovered in a finely divided form consisting of
15 particles of relatively uniform size, e.g., from about 10 to 50 microns.

The color concentrates which may be used in the preparation of the powder colorant compositions comprise crystalline, semi-crystalline and amorphous
20 polyesters having copolymerized therein at least 1.0, preferably at least 5.0, weight percent of the residues of at least one thermally-stable, difunctional colorant compound. The concentration of the colorant residue in the polyester is dependent on such factors as the end
25 use for which a particular concentrate is designed, the polyester being used, and the physical characteristics required of the color concentrate. Normally, the color concentrates will not contain more than about 50 weight percent of colorant residues with a concentration in the
30 range of about 10 to 40 weight percent being more common. Typically, the polyester color concentrates have an inherent viscosity of at least 0.20 and are comprised of (i) a diacid component consisting of the

residues of one or more dicarboxylic acids, (ii) a diol component consisting of the residues of one or more diols and (iii) a colorant component consisting of the residues of one or more thermally-stable, difunctional colorant compounds. The concentration of colorant component (iii) and inherent viscosity are interrelated to the extent that the degree of polymerization and the inherent viscosity should be sufficiently high to ensure that substantially all of the colorant compound is reacted into the polymer and, preferably, into polymer chains which are not extractable. Thus, for example, when the concentration of colorant component (iii) is 20 weight percent or higher, the inherent viscosity of the polyester normally will be about 0.25 or higher.

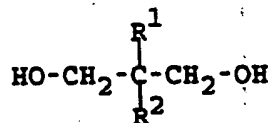
The diacid residues may be derived from aliphatic, alicyclic, or aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, 1,12-dodecanedioic acid, 2,6-naphthalenedicarboxylic acid and the like. In the polymer preparation, it is often preferable to derive the diacid residues from an ester-forming derivative of the dicarboxylic acid such as the dimethyl, diethyl, or dipropyl esters. The anhydrides or acid halides of these acids also may be employed where practical.

The diol components of the described polyesters may be selected from ethylene glycol, 1,2-propanediol, 1,3-propanediol, 2-methyl-1,3-propanediol, 1,4-butanediol, 2,2-dimethyl-1,3-propanediol, 1,6-hexanediol, 1,10-decanediol, 1,12-dodecanediol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol,

- 10 -

2,2,4,4-tetramethyl-1,3-cyclobutanediol, X,8-bis-(hydroxymethyl)-tricyclo-[5.2.1.0]-decane wherein X represents 3, 4, or 5; and diols containing one or more oxygen atoms in the chain, e.g., diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol, 1,3- and 1,4-bis(2-hydroxyethyl)benzene and the like. In general, these diols contain 2 to 18, preferably 2 to 12 carbon atoms. Cycloaliphatic diols can be employed in their cis or trans configuration or as mixtures of both forms.

The preferred amorphous color concentrates from which these powder colorant compositions may be prepared exhibit a glass transition temperature (T_g) and no, or only a trace of, crystallization or melting point by differential scanning calorimetry (DSC). Examples of such amorphous polyesters include those obtained by the polymerization of a difunctional colorant compound, terephthalic and/or 2,6-naphthalenedicarboxylic acid and a branched-chain diol having the formula



wherein R¹ is hydrogen or an unsubstituted or substituted alkyl, cycloalkyl or aryl radical, and R² is an unsubstituted or substituted alkyl, cycloalkyl or aryl radical. Preferred amorphous polyester color concentrates have an inherent viscosity of about 0.2 to 0.8 and are comprised of:

- 11 -

(i) diacid residues comprised of at least 50, preferably at least 80, mole percent terephthalic and/or 2,6-naphthalenedicarboxylic acid residues;

5 (ii) diol residues comprised of at least 50, preferably at least 80, mole percent of residues of a diol having the formula



wherein R^1 is hydrogen or lower alkyl and R^2 is lower alkyl; and

20

(iii) residues of a thermally-stable, difunctional colorant compound.

25 The particularly preferred amorphous polyester color concentrates are comprised of (i) diacid residues consisting essentially of terephthalic and/or 2,6-naphthalenedicarboxylic acid residues; (ii) diol residues consisting essentially of 2,2-dimethyl-1,3-propanediol residues; and (iii) residues of one or more

30 colorant compounds.

Other amorphous polyesters, as defined above, suitable for preparing the powder colorant compositions may be obtained by employing (1) two dicarboxylic acids and one or more diols or (2) two diols and one or more

35 dicarboxylic acids according to known procedures for obtaining amorphous polyesters. The polyester comprising a diacid component consisting of 75 mole percent terephthalic acid residues and 25 mole percent

- 12 -

1,4-cyclohexanedicarboxylic acid residues, a diol component comprised of 1,4-butanediol residues and residues of a difunctional colorant compound of Formula (I) is an example of such a polyester.

5 The partially-crystalline color concentrates useful in the preparation of the powder colorant compositions usually exhibit a glass transition temperature, a crystallization temperature and a melting temperature by DSC. These partially-crystalline, polyester
10 concentrates are comprised of (i) diacid residues consisting of at least 80 mole percent terephthalic acid residues, 2,6-naphthalenedicarboxylic acid residues, 1,3-cyclohexanedicarboxylic acid residues, 1,4-cyclohexanedicarboxylic acid residues or a mixture thereof,
15 (ii) diol residues comprised of at least 50 mole percent of residues having the formula $-O-(CH_2)_p-O-$ wherein p is 2, preferably 4, to 12 and (iii) residues of a thermally-stable, difunctional, colorant compound. A preferred partially-crystalline color concentrate has
20 a melting temperature of at least 110°C and is comprised of (i) diacid residues comprised of at least 80 mole percent terephthalic acid residues, (ii) diol residues comprised of at least 80 mole percent of residues of 1,4-butanediol and (iii) residues of the colorant
25 compound. An especially preferred partially-crystalline color concentrate has a melting temperature of at least 110°C and consists essentially of (i) terephthalic acid residues, (ii) 1,4-butanediol residues and (iii) residues of one of the difunctional, colorant
30 compounds described below.

The polyester color concentrates may be prepared according to conventional esterification or transesterification and melt polycondensation procedures using (i)

- 13 -

a dicarboxylic acid or, preferably, a lower alkyl ester thereof, (ii) a diol and (iii) a thermally stable colorant compound bearing two reactive groups.

Normally, a 50 mol percent excess of the diol is used.

5 The colorant compound preferably is added with the other monomers at the commencement of the color concentrate manufacture although it may be added subsequently, e.g., at the beginning or during the polycondensation step. The concentration (weight
10 percent) of the colorant residue is determined by summing up the weights of all the components charged to the reactor and subtracting the sum of the weights of the components removed during transesterification and polycondensation, e.g., methanol and excess diol. The
15 difference represents the theoretical yield of the color concentrate. The weight of the colorant charged to the reactor is divided by the theoretical weight and multiplied by 100 to give the weight percent of colorant residue.

20 The thermally-stable, difunctional, colorant compounds useful in the preparation of the polyester color concentrates and, thus, the powder colorant compositions may be selected from a wide variety of colorant compounds of diverse structure types and/or
25 classes. The only requirements of useful colorant compounds are that (1) they are stable under polyester polymerization conditions and (2) their structures bear at least two polyester-reactive substituents. Examples of the types or classes of colorant compounds which may
30 be used include methines, bis-methines, anthraquinones, 2,5-diarylamino-terephthalic acids, quinophthalones, thioxanthenes, 3H-dibenz[f,i]isoquinoline-2,7-diones (anthrapyridones), 7H-dibenz[f,i]isoquinoline-7-ones

- 14 -

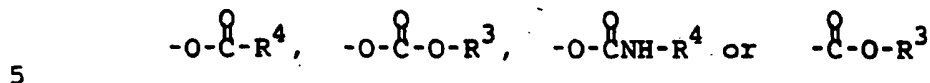
(anthrapyridines), 7H-benz[e]perimidine-7-ones, 7-amino-2H-1-benzopyran-2-ones (coumarins), triphenodioxazines, 5,12-dihydroquinoxalino [2,3-b]phenazines (fluorindines), phthaloylpyrrocolines, 4-amino-
5 naphthalimides, 3,6-diaminopyromellitic acid dimides, benzanthrones, naphtho[1',2',3':4,5]quino[2,1-b]quinazoline-5,10-diones, 6,15-dihydro-5,9,14,18-anthrazinetetrones (indanthrones), 5H-benzo[a]phenoxazine-5-ones, 6H,13H-pyrido[1,2-a:3,4-b] diindole-6,13-
10 diones, diindolo[3,2,1-de-3',2',1'-ij][1,5] naphthyridine-6,13-diones, perylenes, perinones, naphthalene-1,4,5,8-tetracarboxylic acids and diimides, quinacridones and phthalocyanines. Specific examples of suitable colorant compounds are described in U.S.
15 Patents 3,417,048, 3,489,713, 4,080,355, 4,088,650, 4,049,376, 4,116,923, 4,267,306, 4,359,570, 4,403,092, 4,594,400, 4,740,581, 4,745,173, 4,617,373, 4,804,719, 4,808,677 and 4,892,922, incorporated herein by reference, and British Patent 1,225,566.

20 As noted above, the colorant compounds described above may be represented by the formula



25 wherein Col is the residue of one of the types of colorants set forth above and X is a polyester-reactive substituent, i.e., a group reactive with at least one of the monomers from which the polyester is prepared. Examples of the reactive groups which X may represent
30 include hydroxy, carboxy, an ester radical, amino, alkylamino, and the like. The ester radicals may be any radical having the formula

- 15 -



wherein R^3 is selected from unsubstituted or substituted alkyl, cycloalkyl or aryl radicals. R^3 preferably is unsubstituted alkyl, e.g., alkyl of up to about 8 carbon atoms, or phenyl, and most preferably, lower alkyl, e.g., methyl and ethyl. R^4 is hydrogen or selected from those groups listed for R^3 . Reactive group X preferably is hydroxy, carboxy, carbalkoxy, or alkanoyloxy of up to about 4 carbon atoms, e.g., carbomethoxy or acetoxy. Known colorant compounds may, if necessary, be functionalized by the addition thereto of reactive groups represented by X according to known procedures.

The powder colorant compositions described herein may be prepared by a dissolution-crystallization-precipitation process comprising the steps of:

- (1) dissolving in an inert, organic solvent a polyester color concentrate comprising a crystalline or, preferably, a partially crystalline or amorphous polyesters having copolymerized therein at least 1.0, preferably at least 5.0, weight percent of the residues of at least one thermally-stable, difunctional colorant compound, e.g., a compound of formula (I); and
- (2) precipitating from the solution of step (1) the semicrystalline colorant composition in a finely divided form consisting of particles of relatively uniform size, e.g., from about 10 to 50 microns.

- 16 -

If desired, the particle size of the powder colorant compositions obtained from the process may be reduced further by conventional grinding processes.

Typically, step (1) is carried out using a solvent in which the polyester color concentrate is soluble to the extent of at least 100 g concentrate per liter of inert solvent. Examples of solvents in which the amorphous and/or partially-crystalline concentrates may be dissolved include halogenated hydrocarbons such as aliphatic chlorides, e.g., methylene chloride; alkyl carboxylic acid esters containing 3 to about 10 carbon atoms, e.g., ethyl acetate and methyl benzoate; hydrocarbons such as toluene; and ethers such as tetrahydrofuran. We have found methylene chloride to be a particularly effective solvent.

The amount of solvent required may vary substantially depending on the particular inert solvent or combination of inert solvents used, the particular polyester color concentrate used and the temperature at which the dissolution is carried out. Typically, the ratio of the concentrate:solvent (weight:weight) is in the range of about 1:3 to 1:15, preferably about 1:4 to 1:8. The temperature at which the dissolution step is performed may be in the range of about 25°C up to the boiling point of the solvent.

The second step of the process may be accomplished by cooling the step (1) solution, with or without a reduction in the volume of solvent, i.e., either with or without a solution concentration step. Another useful technique involves adding to the step (1) solution a miscible, inert, organic liquid/solvent (usually having a higher boiling point) which causes crystallization and precipitation of the colored semicrystalline powder,

- 17 -

either with or without partial, or essentially complete, removal of the step (1) solvent by distillation. The use of methylene chloride as the step (1) solvent and an alkyl acetate such as ethyl acetate as the "crystallization-inducing" solvent has been found to be particularly efficacious and preferred.

Depending on their intended utility, the powder colorant compositions obtained in accordance with this process may be extracted with a suitable organic solvent to remove relatively low molecular weight polyester oligomers. Examples of oligomer-extracting solvents include ketones such as acetone, 2-pentanone, 3-methyl-2-butanone, 4-methyl-2-pentanone, 2-hexanone and 5-methyl-2-hexanone; hydrocarbons such as hexane, heptane and toluene; and ethers such as tetrahydrofuran. Another, but not preferred, dissolution-precipitation procedure involves dissolving an amorphous color concentrate in certain solvents, e.g., ethyl acetate, from which the polymeric color concentrate, after undergoing a change in morphology, precipitates.

Some of the more crystalline polyesters such as poly(ethylene terephthalate) and poly(tetramethylene terephthalate) require the use of a high-boiling solvent in the dissolution-precipitation procedure. Examples of such high-boiling solvents include alkyl esters of aromatic mono- and di-carboxylic acids, e.g. alkyl benzoates and alkyl phthalates; aliphatic dicarboxylic acid esters; glycol esters, e.g. ethylene glycol diacetate; diethylene glycol diacetate; aromatic ketones, e.g., acetophenone; aromatic oxides, e.g. diphenyl oxide; aliphatic carboxamides, e.g. N,N-dimethylformamide; isophorone. Methyl benzoate and ethylene glycol diacetate are particularly preferred

- 18 -

high-boiling solvents since they are readily available, have a pleasant odor and do not cause color problems during crystallization which sometimes is a problem with the aromatic ketones.

5 In one aspect of this process, a crude polyester color concentrate is prepared and granulated to a very coarse powder which is then heated with a high-boiling solvent, e.g. methyl benzoate, to facilitate dissolution. Upon cooling, crystallization-precipitation
10 occurs and a diluent such as acetone usually is needed to permit stirring. Filtration gives a finely-divided powder which may require washing or reslurrying to remove the crystallization solvent and low molecular weight oligomeric material.

15 In another variation of the dissolution-crystallization-precipitation process, crystallization can occur as an integral part of the polyester color concentrate manufacturing process wherein a high-boiling solvent crystallization solvent is added to a melt of
20 the concentrate to obtain a solution of the color concentrate which then may be obtained as a powder by precipitation. The polyester color concentrate powder is thus obtained in a purified form without the need of a granulation step by a means which may be used in
25 conjunction with batch processing. The solvent used in this embodiment normally should have a boiling point of at least 120°C, preferably in the range of about 150 to 275°C. Examples of such high-boiling inert solvents
30 include lower alkyl, e.g., alkyl of up to about 4 carbon atoms, esters of aromatic mono- and di-carboxylic acids such as methyl benzoate, butyl benzoate, dimethyl phthalate; glycol esters, e.g., ethylene glycol diacetate; aromatic ethers such as diphenyl oxide;

- 19 -

alkanoyl benzenes, such as acetophenone; and glycol ethers.

The dissolution-crystallization-precipitation procedure alters the morphology of the amorphous and partially-crystalline polyester color concentrates in a number of respects. X-Ray diffraction analysis of the colored semicrystalline powders shows a marked increase in the crystallinity of the polyester and, while the amorphous polyester concentrates do not exhibit a melting temperature, the microcrystalline concentrates usually (almost always) exhibit a melting temperature by DSC. Although the weight average molecular weight (M_w) may either increase or not be changed by the dissolution-crystallization-precipitation procedure, the number average molecular weight (M_n) always increases, the magnitude of the increase depending on the degree to which oligomeric material has been removed from the colored semicrystalline polyester powder. The polydispersity ratio ($M_w:M_n$) of the colored semicrystalline polyester is always less than that of the polyester concentrate from which it is prepared due to the increase in M_n (even when M_w increases, M_n increases more). Finally, the inherent viscosity of the colored semicrystalline powders normally is slightly higher than that of the corresponding color concentrates.

A multiplicity of colors of semicrystalline polyester powders may be obtained by combining individual colors, e.g., subtractive colors such as yellow, magenta and cyan according to known color technology (see N. Ohta, Photographic Science and Engineering, Volume 15, No. 5, Sept.-Oct. 1971, pp. 399-415). In the practice of this invention the colors may be combined at various

- 20 -

appropriate stages in the preparation of the semi-crystalline powders:

- 5 (a) two or more copolymerizable colorants are added to the initial polymerization reaction; upon completion of the polycondensation reaction the colored semicrystalline powder is prepared via the above-mentioned dissolution-crystallization-precipitation procedure;
- 10 (b) two or more colored amorphous or partially crystalline color concentrates are combined and then converted to a colored semi-crystalline polyester powder via the
- 15 dissolution-crystallization-precipitation;
- (c) two or more colored semicrystalline polyester powders are combined and the dissolution-crystallization-precipitation procedure
- 20 repeated; or
- (d) two or more colored semicrystalline polyester powders are physically admixed by using known blending methods.

25

The colored polyesters of U.S. Serial No. 07/604,311 may possess one or more difunctional colorants or may exist as a mixture of polyester compositions, each possessing one or more difunctional colorants. Further, two or

30 more colored polyesters containing at least one difunctional colorant copolymerized therein may be combined in their amorphous, partially crystalline or semi-crystalline powder forms and added to the thermo-

- 21 -

plastic polymers using known methods. Also, as well understood by those skilled in the art, conventional additives may be present in the colored semicrystalline polyester powder compositions. For instance, such
5 additives may include plasticizers, flame retardants, nucleating agents, lubricants, stabilizers, processing aids, fillers, antioxidants or opacifiers such as titanium dioxide.

A wide range of thermoplastic polymers useful for
10 blending with the polyester color concentrates in the practice of the present invention are known in the art and includes homopolymers and copolymers of polyesters e.g., poly(ethylene terephthalate); polyolefins, e.g., polypropylene, polyethylene, linear low density poly-
15 ethylene, polybutylene and copolymers made from ethylene, propylene and/or butylene; copolymers from acrylonitrile, butadiene and styrene; copolymers from styrene and acrylonitrile; polyamides, e.g., Nylon 6 and Nylon 66; polyvinyl chloride; polyurethanes; poly-
20 vinylidene chloride; polycarbonates; cellulose esters, e.g., cellulose acetate, propionate, butyrate or mixed esters; polyacrylates, e.g., poly(methyl methacrylate); polyimides; polyester-amides; polystyrene; etc.

According to the invention the colored polyesters
25 are incorporated into the thermoplastic polymers using conventional techniques, e.g., solution or melt-blending, such as those employed to incorporate other additives in such resins (see R. Gächter and H. Müller, Editors, *Plastics Additives Handbook*, Hansu Publishers, New York, 1985, pp 507-533; 729-741). For example, the
30 colored polyester compositions may be dry blended in form of powders or pellets with the thermoplastic resin in the form of pellets or ground powders with or without

- 22 -

an adhesion promoter or a dispersing agent. This premix can be subsequently processed on extruders or injection molding machines.

5 As a general proposition, it is known that attempts to blend polyesters with other thermoplastic polymers often result in a blend with inferior physical properties. (See, for example, Encyclopedia of Polymer Science and Engineering, Vol. 12, p. 399, Ed. by H. F. Mack et al, John Wiley and Sons, Inc., New York (1988).)

10 However, the present invention provides colored polymeric thermoplastic blends wherein the blends do not appreciably differ in physical properties from the discrete polymers.

15 The particular chromophore groups present will, of course, determine the color (hue + value + chroma) of the polyester composition and finally the color (hue + value + chroma) of the thermoplastic or polymer blends of the invention. A large gamut of colors may be obtained by blending two or more polyester colorant
20 compositions with the thermoplastic resin to be colored, followed by molding or extruding or by first blending two or more polyester colorant compositions together and then blending these premixed materials with the thermoplastic polymer or polymers to be
25 colored. Alternatively, a concentrate of the polyester colorant compositions in an appropriate vehicle may be prepared. The concentrate may be in the form of liquids, pastes, slurries, or solids, e.g., powders, compacted powders, pellets, etc., and may be
30 incorporated by known methods into the thermoplastic polymer(s).

The actual amount of the colored polyester composition used to color the thermoplastic polymer will

- 23 -

depend upon the inherent tinctorial strength of the copolymerized colorant, the weight percent of the colorant in the colored polyester composition and the desired depth of shade. Typically, the amount of polyester color concentrate added to the thermoplastic polymer is such that the total amount of colorant residue present by weight in the final thermoplastic polymer blend composition is from about 0.001% to about 10%, preferably from about 0.01% to about 5%.

10 The colored thermoplastic polymer compositions provided by the present invention are useful as thick and thin plastic films, extruded coatings and lamination layers, plastic sheeting, molded plastic articles and fibers.

15 The Experimental Section below further describes the present invention but is in no fashion intended to limit the scope thereof. The inherent viscosities specified herein are determined at 25°C using 0.5 g of polymer per 100 mL of a solvent consisting of 60 weight percent phenol and 40 weight percent tetrachloroethane. 20 The weight average molecular weight (Mw) and number average molecular weight (Mn) values referred to herein are determined by gel permeation chromatography. The melting temperatures are determined by differential scanning calorimetry on the first and/or second heating 25 cycle at a scanning rate of 20°C per minute and are reported as the peaks of the transitions.

Experimental Section

30

Preparation 1

The following materials were charged to the reactor:

- 24 -

12.47 lbs (62.8 mol) 1,4-butanediol

1.50 lbs (1.42 mol) 1,5-bis(carboxyanilino)-anthraquinone

10

The jacketed reactor was equipped with a nitrogen inlet, stirrer, vacuum outlet, and condenser, and was heated by oil circulating through the jacket. The reactor was continuously purged with nitrogen while the contents of the reactor were heated to 180°C over two hours. The temperature was held for 30 minutes at 180°C, then increased to 200°C over 30 minutes. The temperature was held for 30 minutes at 200°C, then increased to 220°C over 20 minutes. Over the next 90 minutes the temperature was increased to 230°C and a vacuum applied until the pressure was reduced to 4000 microns Hg. The polycondensation was completed by holding the reactor contents at 230°C and about 4000 microns Hg pressure for 30 minutes. The reactor was then pressurized with nitrogen to extrude the contents of the reactor into water. The extruded polymer was granulated by grinding to a particle size of about 3 mm in a Wiley mill, then dried under vacuum at 80°C for four hours.

The resulting dark red polyester contains approximately 10 weight percent of the anthraquinone colorant residue and has an inherent viscosity of 0.36, a melting temperature of 218°C, a weight average molecular weight of 20,480, a number average molecular weight of 14,789 and a polydispersity value of 1.51.

- 25 -

Preparation 2

The following materials were charged to the reactor:

- 5 11.90 lbs (27.8 mol) dimethyl terephthalate
- 12.47 lbs (62.8 mol) 1,4-butanediol
- 14.58 g Ti from a n-butanol solution of titanium
- 10 tetraisopropoxide
- 1.50 lbs (1.42 mol) 1,5-bis(carboxyanilino)-
- anthraquinone

15

The jacketed reactor was equipped with a nitrogen inlet, stirrer, vacuum outlet, and condenser, and was heated by oil circulating through the jacket. The reactor was continuously purged with nitrogen while the contents of the reactor were heated to 180°C over two hours. The temperature was held for 30 minutes at 180°C, then increased to 200°C over 30 minutes. The temperature was held for 30 minutes at 200°C, then increased to 220°C over 20 minutes. Over the next 90 minutes the temperature was increased to 230°C and a vacuum applied until the pressure was reduced to approximately 3800 microns Hg. The polycondensation was completed by holding the reactor contents at 230°C for two hours and reducing the pressure to about 1000 microns Hg. The reactor was then pressurized with nitrogen to extrude the contents of the reactor into water. The extruded polymer was granulated by grinding to a particle size of about 3 mm in a Wiley mill, then dried under vacuum at 80°C for four hours.

The resulting dark red polyester contains about 10% by weight of the anthraquinone color and residue and has

- 26 -

an inherent viscosity of 0.64, a melting temperature of 218°C, a weight average molecular weight of 36,676, a number average molecular weight of 21,202 and a polydispersity of 1.71.

5

Preparation 3

The following materials were charged to the reactor:

- 10 11.90 lbs (27.8 mol) dimethyl terephthalate
- 12.47 lbs (62.8 mol) 1,4-butanediol
- 14.58 g Ti from a n-butanol solution of titanium
- 15 tetraisopropoxide
- 1.50 lbs 1,5-bis(carboxyphenylthio)anthraquinone

20

The jacketed reactor was equipped with a nitrogen inlet, stirrer, vacuum outlet, and condenser, and was heated by oil circulating through the jacket. The reactor was continuously purged with nitrogen while the

25 contents of the reactor were heated to 180°C over two hours. The temperature was held for 30 minutes at 180°C, then increased to 200°C over 30 minutes. The temperature was held for 30 minutes at 200°C, then increased to 220°C over 20 minutes. Over the next 90

30 minutes the temperature was increased to 230°C and a vacuum was applied until the pressure was reduced to 4000 microns Hg. The polycondensation was completed by holding the reactor contents at 230°C for 30 minutes while reducing the pressure to about 1400 microns Hg.

35 The reactor was then pressurized with nitrogen to extrude the contents of the reactor into water. The

- 27 -

extruded polymer was granulated by grinding in a Wiley mill, then dried under vacuum at 80°C for four hours.

The resulting dark yellow polymer contains approximately 10 weight percent of the anthraquinone colorant residue and has an inherent viscosity of 0.27, a melting temperature of 214°C, a weight average molecular weight of 14,533, a number average molecular weight of 9,941 and a polydispersity of 1.46.

10 Preparation 4

The following materials were charged to the reactor:

- 15 11.90 lbs (27.8 mol) dimethyl terephthalate
- 12.47 lbs (62.8 mol) 1,4-butanediol
- 14.58 g Ti from a n-butanol solution of titanium tetraisopropoxide
- 20 1.50 lbs 1,5-bis(carboxyphenylthio)anthraquinone

25 The jacketed reactor was equipped with a nitrogen inlet, stirrer, vacuum outlet, and condenser, and was heated by oil circulating through the jacket. The reactor was continuously purged with nitrogen while the contents of the reactor were heated to 180°C over two hours. The temperature was held for 30 minutes at 180°C, then increased to 200°C over 30 minutes. The temperature was held for 30 minutes at 200°C, then increased to 220°C over 20 minutes. Over the next 90 minutes the temperature was increased to 230°C and a vacuum was applied until the pressure was reduced to 3900 microns Hg. The polycondensation was completed by holding the reactor contents at 230° for two hours while

- 28 -

reducing the pressure to about 550 microns. The reactor was then pressurized with nitrogen to extrude the contents of the reactor into water. The extruded polymer was granulated by grinding in a Wiley mill, then
5 dried under vacuum at 80°C for four hours.

The dark yellow polyester concentrate has an inherent viscosity of 0.79, a melting temperature of 218°C, a weight average molecular weight of 46,778, a number average molecular weight of 25,347, a poly-
10 dispersity of 1.84 and contains about 10 weight percent of the anthraquinone colorant residue.

Preparation 5

The following materials were placed in a 500-mL
15 three-necked, round-bottom flask:

155.2 g (0.80 mol) dimethyl terephthalate

108.0 g (1.20 mol) 1,4-butanediol

20 0.0226 g Ti from a n-butanol solution of titanium tetraisopropoxide

25 80.0 g (0.212 mol) methyl 3-[4-[[2-acetyloxy]-ethylamino]-2-methylphenyl]-2-cyano-2-propenoate)

30 The flask was equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents were heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature was increased to 200°C and then to 220°C over two
35 hours. Over the next 1.0 hour, the temperature was increased to about 240°C and a vacuum applied until the pressure was reduced to 0.5 mm Hg. The polycondensation

- 29 -

was completed by heating the flask and contents at about 240°C for 30 minutes under a pressure of 0.1 to 0.5 mm Hg. The vacuum was then relieved with nitrogen and methyl benzoate (145 mL) added slowly and stirred to solution over about 10 minutes with the flask still in the metal bath. The resulting solution was transferred to a 2 L beaker and stirred until crystallization occurred. Acetone (700 mL) was added slowly with stirring to dilute the slurry and keep it stirrable. The diluted slurry was stirred for 30 minutes, filtered and the cake washed with acetone. The cake was twice reslurried in acetone and then dried in air. The resulting dark yellow semicrystalline polyester powder, containing 30.87 wt % of the methine colorant residue, has an inherent viscosity of 0.224, a melting temperature of 189°C, a weight average molecular weight of 11,112, a number average molecular weight of 8,117 and a polydispersity value of 1.37. The weight of recovered powder is 197.0 g.

20

Preparation 6

The following materials were placed in a 500-mL three-necked, round-bottom flask:

25 80.44 g (0.415 m) dimethyl terephthalate
 67.67 g (0.752 m) 1,4-butanediol
 0.0137 g Ti from a n-butanol solution of titanium
30 tetraisopropoxide
 41.42 g (0.0866 m) 1,5-bis(2-carboxyanilino)
 anthraquinone

35

- 30 -

The flask was equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents were heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the

5 temperature was increased to 200°C and then to 220°C over two hours. Over the next 30 minutes the temperature was increased to about 245°C and then to about 260°C over the next 30 minutes. The temperature was quickly raised (over about 10 minutes) to 270°C and a

10 vacuum applied until the pressure was reduced to 0.5 mm Hg. The polycondensation was completed by heating the flask and contents at about 270°C for 10 minutes under a pressure of 0.1 to 0.5 mm Hg. The vacuum was then relieved with nitrogen and methyl benzoate (125 mL) was

15 added slowly and stirred to solution over about 10 minutes with the flask still in the metal bath. The resulting solution was transferred to a 2 L beaker and stirred until crystallization occurs. Hexane (700 mL) was added slowly with stirring to dilute the slurry and

20 keep it stirrable. The diluted slurry was stirred for 30 minutes, filtered and the cake washed with hexane. The cake was twice reslurried in acetone and then dried in air. The resulting dark red semicrystalline polyester powder, containing 30.16 wt % of the anthra-

25 quinone colorant residue, has an inherent viscosity of 0.214, a melting temperature of 196°C, a weight average molecular weight of 12,557, a number average molecular weight of 7,805 and a polydispersity value of 1.61. The weight of recovered powder was 132 g.

30

Preparation 7

The following materials were placed in a 500-mL three-necked, round-bottom flask:

- 31 -

116.4 g (0.60 mol) dimethyl terephthalate

81.0 g (0.90 mol) 1,4-butanediol

5 0.0143 g Ti from a n-butanol solution of titanium
 tetraisopropoxide

10 14.25 g (0.0347 mol) 1,5-bis[(3-hydroxy-2,2-
 dimethylpropyl)amino]anthraquinone

 The flask was equipped with a nitrogen inlet,
 stirrer, vacuum outlet, and condensing flask. The flask
15 and contents were heated in a Belmont metal bath with a
 nitrogen sweep over the reaction mixture as the
 temperature was increased to 200°C and then to 230°C
 over two hours. Over the next 1.0 hour the temperature
 was increased to about 260°C. The polycondensation was
20 completed by heating the flask and contents at about
 260°C for 15 minutes under a pressure of 0.1 to 0.5 mm
 Hg. The vacuum was then relieved with nitrogen and
 methyl benzoate (125 mL) was added slowly and stirred
 to solution over about 10 minutes with the flask still
25 in the metal bath. The resulting solution was trans-
 ferred to a 2L beaker and stirred until crystallization
 occurs. Acetone (700 mL) was added slowly with stirring
 to dilute the slurry and keep it stirrable. The diluted
 slurry was stirred for 30 minutes, filtered and the cake
30 was washed with acetone. The cake was twice reslurried
 in acetone and then dried in air. The resulting dark
 red semicrystalline polyester powder, containing
 9.96 wt % of the anthraquinone colorant residue, has an
 inherent viscosity of 0.265, a melting temperature of
35 213°C, a weight average molecular weight of 13,361, a
 number average molecular weight of 9,278 and a poly-
 dispersity value of 1.44.

- 32 -

Preparation 8

The following materials were placed in a 500 mL three-necked, round-bottom flask:

- 5 107.40 g (0.554 m) dimethyl terephthalate
 81.00 g (0.90 mol) 1,4-butanediol
 0.0146 g Ti from a n-butanol solution of titanium
10 tetraisopropoxide
 23.0 g (0.0464 m) red anthrapyridone colorant
 having the formula

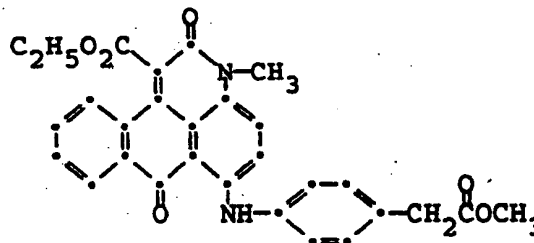
15

20

25

30

35



- The flask was equipped with a nitrogen inlet,
 stirrer, vacuum outlet, and condensing flask. The flask
40 and contents were heated in a Belmont metal bath with a
 nitrogen sweep over the reaction mixture as the
 temperature was increased to 200°C and then to 230°C
 over two hours. The temperature was quickly raised
 (over about 10 minutes) to 240°C and a vacuum was
45 applied until the pressure was reduced to 0.5 mm Hg.
 The polycondensation was completed by heating the flask
 and contents at about 240°C for 1.0 hour under a
 pressure of 0.1 to 0.5 mm Hg. The vacuum was then
 relieved with nitrogen and methyl benzoate (125 mL) was
50 added slowly and stirred to solution over about 10
 minutes with the flask still in the metal bath. The

- 33 -

resulting solution was transferred to a 2 L beaker and stirred until crystallization occurs. Acetone (700 mL) was added slowly with stirring to dilute the slurry and keep it stirrable. The diluted slurry was stirred for 5 30 minutes, filtered and the cake was washed with acetone. The cake was twice reslurried in acetone and then dried in air. The resulting dark red semi-crystalline polyester powder, containing 15.75 wt % of the anthrapyridone colorant residue, has an inherent 10 viscosity of 0.25, a melting temperature of 214°C, a weight average molecular weight of 14,074, a number average molecular weight of 9,410 and a polydispersity value of 1.49. The weight of recovered powder is 135.6 g.

15

Preparation 9

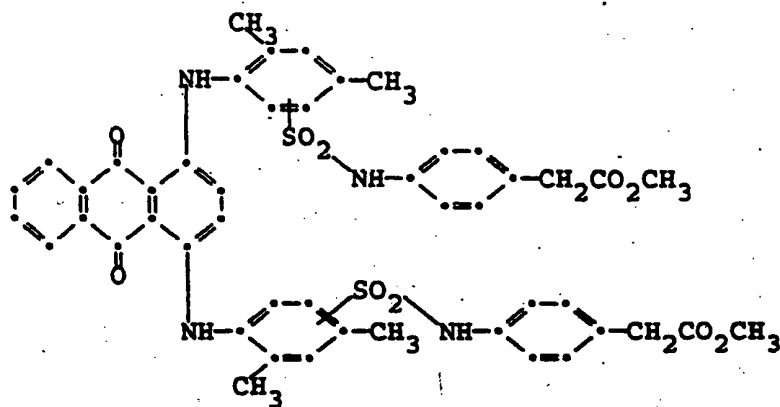
The following materials were placed in a 500 mL three-necked, round-bottom flask:

20 56.64 g (0.39 m) dimethyl terephthalate
 40.50 g (0.45 m) 1,4-butanediol
 .0072 g Ti from a n-butanol solution of titanium
25 tetraisopropoxide
 7.25 g (0.00805 m) blue anthraquinone colorant
 having the formula

30

- 34 -

5
10
15
20
25
30



The flask was equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents were heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature was increased to 200°C and then to 220°C over two hours. Over the next 2.5 hours the temperature was increased to about 230°C and a vacuum was applied until the pressure was reduced to 0.5 mm Hg. The polycondensation was completed by heating the flask and contents at about 230°C for 20 minutes under a pressure of 0.1 to 0.5 mm Hg. The vacuum was then relieved with nitrogen and methyl benzoate (60 mL) was added slowly and stirred to solution over about 10 minutes with the flask still in the metal bath. The resulting solution was transferred to a 2 L beaker and stirred until crystallization occurs. Acetone (350 mL) was added slowly with stirring to dilute the slurry and keep it stirrable. The diluted slurry was stirred for 30 minutes, filtered and the cake was washed with hexane three times and then dried in air. The resulting dark blue semicrystalline polyester powder, containing 10.1 wt % of the anthraquinone colorant residue, has an

- 35 -

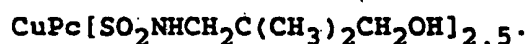
inherent viscosity of 0.188. The weight of recovered powder of 68.6 g.

Preparation 10

5 A sample (300 g, 30% solids - 100 g dry basis) of water-wet copper phthalocyaninesulfonyl chloride containing an average of about 2.5 sulfonyl chloride groups per molecule was added to a stirred beaker containing tetrahydrofuran (500 mL) and 3-amino-2,2-
10 dimethylpropanol (100 mL) with good stirring to facilitate solution with external ice-water cooling at about 0-5°C. The reaction mixture was allowed to warm gradually to room temperature and stirring continued for about 12 hours and then drowned into 2L of dilute
15 hydrochloric acid (pH <5-6). The blue solid was collected by filtration and the wet filter cake reslurried in 2L of 5% hydrochloric acid and filtered with vacuum. Most of the water was removed by vacuum
20 filtration and air drying and then the still somewhat moist filter cake was added to tetrahydrofuran (250 mL) and the tetrahydrofuran and water removed under vacuum to leave a fairly dry product. This product when
25 analyzed by thin-layer chromatography showed a small amount of very polar by-product presumed to be some of the sulfonic acid derivative. This compound can be used without further purification to impart color to poly-
30 esters by copolymerization particularly when used at lower levels even with some sulfonic acid derivative present. Further purification to remove most of the sulfonic acid derivative was accomplished by dissolving a portion (25 g) of the crude material in tetra-
hydrofuran (100 mL) followed by chromatography through activated magnesium silicate in a coarse glass-fritted

- 36 -

funnel using methylene chloride followed by methylene chloride:tetrahydrofuran (50:50 v/v) for elution until no more blue color is eluted. The eluents were combined and the solvent removed under vacuum to leave the cyan product (18.8 g) essentially free of any sulfonic acid derivative largely represented by the formula:



10 Preparation 11

The following materials were placed in a 500 mL, three-necked, round-bottom flask:

15 81.38 g (0.419 mol) dimethyl terephthalate

68.00 g (0.755 mol) 1,4-butanediol

0.0139 g Ti from a n-butanol solution of titanium tetraisopropoxide

20 43.10 g (0.0842 mol) 1,5-bis(o-carboxyphenylthio)-anthraquinone

25 The flask was equipped with a nitrogen inlet, stirrer vacuum outlet, and condensing flask. The flask and contents were heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the
30 temperature was increased to 200°C and then to 220°C over 2 hours. Over the next 30 minutes the temperature was increased to about 240°C and then to about 260°C over the next 30 minutes. The temperature was quickly
35 raised (over about 10 minutes) to 275°C and a vacuum was applied until the pressure was reduced to 0.5 mm Hg. The polycondensation was completed by heating the flask and contents at about 275°C for 5 minutes under a

- 37 -

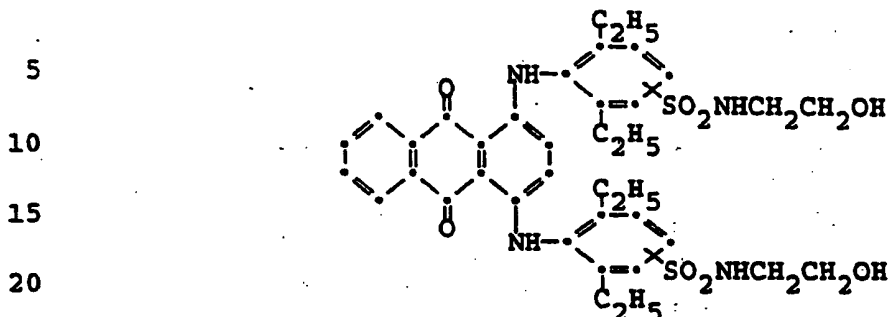
pressure of 0.1 to 0.5 mm Hg. The vacuum was then relieved with nitrogen and methyl benzoate (125 mL) was added slowly and stirred to solution over about 10 minutes with the flask still in the metal bath. The resulting solution was transferred to a 2 L beaker and stirred until crystallization occurs. Acetone:hexane (1:1 by volume) mixture (1.0 L) was added slowly with stirring to dilute the slurry and keep it stirrable. The diluted slurry was stirred for 30 minutes, filtered and the cake was washed with acetone:hexane (1:1) mixture. The cake was twice reslurried in acetone and then dried in air. The resulting yellow semicrystalline polyester powder, containing 30.79 weight percent of the anthraquinone colorant residue, had an inherent viscosity of 0.12, a melting temperature of 178°C, a weight average molecular weight of 8,500, a number average molecular weight of 6,477 and a polydispersity value of 1.31. The weight of recovered powder was 122 g.

Preparation 12

The following materials were placed in a 500 mL, three-necked, round-bottom flask:

58.20 g (0.30 mol) dimethyl terephthalate
40.50 g (0.45 mol) 1,4-butanediol
0.0075 g Ti from a n-butanol solution of titanium tetraisopropoxide
22.0 g (0.029 mol) blue anthraquinone colorant having the formula:

- 38 -



25 The flask was equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents were heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the

30 temperature was increased to 200° and then to 220° over 2 hours. Over the next 30 minutes the temperature was increased to about 240° and then to about 260° over the next 30 minutes. The temperature was quickly raised

35 (over about 10 minutes) to 275° and a vacuum was applied until the pressure is reduced to 0.5 mm Hg. The polycondensation was completed by heating the flask and contents at about 275°C for 5 minutes under a pressure

40 of 0.1 to 0.5 mm Hg. The vacuum was then relieved with nitrogen and methyl benzoate (100 mL) was added slowly and stirred to solution over about 10 minutes with the flask still in the metal bath. The resulting solution

45 was transferred to a 2 L beaker and stirred until crystallization occurs. Hexane (700 mL) was added slowly with stirring to dilute the slurry and keep it stirrable. The diluted slurry was stirred for

50 30 minutes, filtered and the cake was washed with hexane three times and then dried in air. The resulting dark blue semicrystalline polyester powder, containing 25.76 weight percent of the anthraquinone colorant residue, had an inherent viscosity of 0.103, a melting tempera-

- 39 -

ture of 182°C, a weight average molecular weight of 4,181, a number average molecular weight of 1.855 and a polydispersity value of 2.25. The weight of recovered powder was 74.4 g.

5

Preparation 13

The following materials were placed in a 500 mL three-necked, round-bottom flask:

10

110.8 g (0.571 mol) dimethyl terephthalate

81.0 g (0.90 mol) 1,4-butanediol

15

0.0141 g Ti from a n-butanol solution of titanium isopropoxide

14.5 g (0.0285 m) red methine colorant having the formula

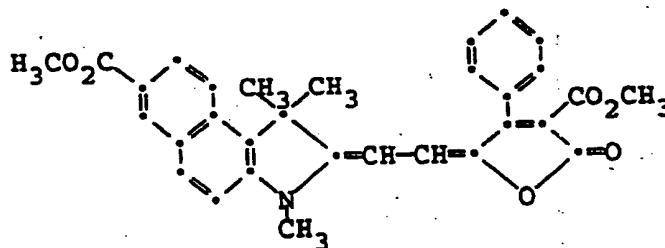
20

25

30

35

40



45

50

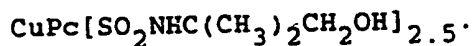
The flask was equipped with a nitrogen inlet, stirrer, vacuum outlet and condensing flask. The flask and contents were heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature was increased to 200°C and then to 230°C over 2.25 hours. Vacuum was applied until the pressure was reduced to about 0.5 mm Hg and the temperature held at 230°C for 30 minutes with the pressure remaining at 0.1-0.5 mm Hg. The vacuum was then relieved with

- 40 -

nitrogen and methyl benzoate (125 mL) was added slowly and stirring continued for 5 minutes to complete solution with the flask still in the metal bath. The resulting solution was transferred to a 2L beaker and stirred until crystallization occurred. Acetone (700 mL) was added slowly with stirring to dilute the slurry and keep it stirrable. The diluted slurry was stirred for about 10 minutes, filtered and the cake washed with acetone. The cake was thrice reslurried in acetone and then dried in a vacuum oven at 50°C for 48 hours. The resulting dark red semicrystalline polyester powder, containing 10.3 wt % of the methine colorant residue, has an inherent viscosity of 0.31, a melting temperature of 220°C, a weight average molecular weight of 17,264, a member average molecular weight of 12,546 and a polydispersity value of 1.38. The weight of recovered powder was 128.5 g.

Preparation 14

A sample (300 g, 30% solids - 100 g dry basis) of water-wet copper phthalocyaninesulfonyl chloride containing an average of about 2.5 sulfonyl chloride groups per molecule was reacted with 2-amino-2-methyl-1-propanol (100 mL), as described in Preparation 10 and the product chromatographed similarly to give a copper phthalocyanine (CuPc) sulfonamide derivative largely represented by the formula:



Preparation 15

The following materials are placed in a 500 mL three-necked, round-bottom flask:

- 41 -

116.40 g (0.60 m) dimethyl terephthalate

81.00 g (0.90 m) 1,4-butanediol

5 0.0145 g Ti from a n-butanol solution of titanium
 tetraisopropoxide

10 14.5 g colorant of Preparation 14 (9.98% by
 weight)

15 The flask was equipped with a nitrogen inlet,
 stirrer, vacuum outlet, and condensing flask. The flask
 and contents were heated in a Belmont metal bath with a
 nitrogen sweep over the reaction mixture as the
 temperature was increased to 200°C and then to 220°C
 over 2 hours. Over the next 1 hour the temperature was
20 increased to about 240°C and then to about 250°C over
 the next 15 minutes. Vacuum was applied until the
 pressure was reduced to 0.5 mm Hg and the poly-
 condensation was completed by heating the flask and
 contents at about 250°C for 45 minutes under a pressure
 of 0.1 to 0.5 mm Hg. The vacuum was then relieved with
25 nitrogen and methyl benzoate (125 mL) was added slowly
 and stirred to solution over about 10 minutes with the
 flask still in the metal bath. The resulting solution
 was transferred to a 2L beaker and stirred until
 crystallization occurred. Acetone (500 mL) was added
30 slowly with stirring to dilute the slurry and keep it
 stirrable. The diluted slurry was stirred for
 30 minutes, filtered and the cake washed with acetone.
 The cake was twice reslurried in acetone and then dried
 in vacuum oven at 50°C. The resulting blue semi-
35 crystalline polyester powder, containing 9.98 weight
 percent of the copper phthalocyanine sulfonamide
 colorant residue, had an inherent viscosity of 0.397, a

- 42 -

melting temperature of 218°C, a weight average molecular weight of 25,536, a number of average molecular weight of 15,930 and a polydispersity value of 1.60. Yield = 137 g (94.3% of the theoretical yield).

5

Preparation 16

The following materials were placed in a 2 L three-necked, round-bottom flask:

- 10 368.60 g (1.90 m) dimethyl terephthalate
 256.50 g (2.85 m) 1,4-butanediol
 0.0509 g Ti from a n-butanol solution of titanium
15 tetraisopropoxide
 100.0 g colorant of Preparation 10 (19.62% by
 weight)

20

- The flask was equipped with a nitrogen inlet,
 stirrer, vacuum outlet, and condensing flask. The flask
 and contents were heated in a Belmont metal bath with a
25 nitrogen sweep over the reaction mixture as the
 temperature was increased to 200°C and then to 220°C
 over 2 hours. Over the next 3 hours the temperature was
 increased to about 230°C. Vacuum was applied until the
 pressure was reduced to 0.5 mm Hg and the polycondensa-
30 tion was then completed by heating the flask and
 contents at about 230°C for 30 minutes under a pressure
 of 0.1 to 0.5 mm Hg. The vacuum was then relieved with
 nitrogen and methyl benzoate (420 mL) added slowly and
 stirred to solution over about 10 minutes with the flask
35 still in the metal bath. The resulting solution was
 transferred to a 4L beaker and stirred until
 crystallization occurred. Acetone (2 L) was added

- 43 -

slowly with stirring to dilute the slurry and keep it stirrable. The diluted slurry was stirred for 30 minutes, filtered and the cake washed with acetone. The cake was twice reslurried in acetone and then dried in vacuum oven at 50°C. The resulting blue semi-crystalline polyester powder, containing 19.62 weight percent of the copper phthalocyanine sulfonamide colorant residue, had an inherent viscosity of 0.425, a melting temperature of 208°C, a weight average molecular weight of 46,248, a number of average molecular weight of 14,150 and a polydispersity value of 3.3. The yield was 491 g (96.4% of the theoretical yield).

Preparation 17

The following materials were placed in a 500 mL, three-necked, round-bottom flask:

110.64 g (0.570 mol) dimethyl terephthalate
81.00 g (0.900 mol) 1,4-butanediol
0.0141 g Ti from a n-butanol solution of titanium tetraisopropoxide
14.20 g (0.0297 mol) 1,5-bis(2-carboxyanilino)-anthraquinone

The flask was equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents were heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature was increased to 200°C and then to 225°C over 2 hours. Over the next 30 minutes the temperature was increased to about 240°C and then to about 250°C over the next 30 minutes. Vacuum was applied until the

- 44 -

pressure was reduced to 0.5 mm Hg. The polycondensation was completed by heating the flask and contents at about 250°C for 1 hour under a pressure of 0.1 to 0.5 mm Hg. The vacuum was then relieved with nitrogen and methyl benzoate (125 mL) was added slowly and stirred to solution over about 10 minutes with the flask still in the metal bath. The resulting solution was transferred to a 2 L beaker and stirred until crystallization occurred. Acetone (700 mL) was added slowly with stirring to dilute the slurry and keep it stirrable. The diluted slurry was stirred for 30 minutes, filtered and the cake was washed with acetone. The cake was twice reslurried in acetone and then dried in air. The resulting dark red semicrystalline polyester powder, containing 10.0 weight percent of the anthraquinone colorant residue, had an inherent viscosity of 0.395, a melting temperature of 217°C, a weight average molecular weight of 22,742, a number average molecular weight of 15,844 and a polydispersity value of 1.43. The weight of recovered powder was 130 g.

Preparation 18

The following materials were placed in a 500-mL three-necked, round-bottom flask:

25

110.98 g (0.572 mol) dimethyl terephthalate

81.0 g (0.90 mol) 1,4-butanediol

30

0.0142 g Ti from a n-butanol solution of titanium tetraisopropoxide

14.30 g (0.0279 mol) 1,5-bis(o-carboxyphenylthio)-anthraquinone

35

- 45 -

The flask was equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents were heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the

5 temperature was increased to 200°C and then to 220°C over 2 hours. Over the next 30 minutes the temperature was increased to about 240°C and then to about 250°C over the next 30 minutes. Vacuum was applied until the pressure was reduced to 0.5 mm Hg. The polycondensation

10 was completed by heating the flask and contents at about 250°C for 1 hour under a pressure of 0.1 to 0.5 mm Hg. The vacuum was then relieved with nitrogen and methyl benzoate (125 mL) was added slowly and stirred to solution over about 10 minutes with the flask still in

15 the metal bath. The resulting solution was transferred to a 2 L beaker and stirred until crystallization occurred. Acetone (700 mL) was added slowly with stirring to dilute the slurry and keep it stirrable. The diluted slurry was stirred for 30 minutes, filtered

20 and the cake was washed with acetone. The cake was twice reslurried in acetone and then dried in air. The resulting yellow semicrystalline polyester powder, containing 10.0 weight percent of the anthraquinone

25 colorant residue, had an inherent viscosity of 0.50, a melting temperature of 217°C, a weight average molecular weight of 27,747, a number average molecular weight of 18,998 and a polydispersity value of 1.46. The yield was 491 g.

30 Preparation 19

The following materials were placed in a 500-mL three-necked, round-bottom flask:

- 46 -

97.00 g (0.50 mol) dimethyl terephthalate

67.50 g (0.75 mol) 1,4-butanediol

5 0.0130 g Ti from a n-butanol solution of titanium
 tetraisopropoxide

10 26.00 (0.0634 mol) 1,5-bis[(3-hydroxy-2,2-
 dimethylpropyl)amino]anthraquinone

15 The flask was equipped with a nitrogen inlet,
 stirrer, vacuum outlet, and condensing flask. The
 flask and contents were heated in a Belmont metal bath
 with a nitrogen sweep over the reaction mixture as the
 temperature was increased to 200°C and then to 220°C
 over 2 hours. Over the next 30 minutes the temperature
 was increased to about 255°C and then to about 260°C
20 over the next 30 minutes. Vacuum was applied until the
 pressure was reduced to 0.5 mm Hg. The polycondensation
 was completed by heating the flask and contents at about
 270°C for 45 minutes under a pressure of 0.1 to 0.5 mm
 Hg. The vacuum was then relieved with nitrogen and
25 methyl benzoate (125 mL) was added slowly and stirred to
 solution over about 10 minutes with the flask still in
 the metal bath. The resulting solution was transferred
 to a 2 L beaker and stirred until crystallization
 occurs. Acetone (700 mL) was added slowly with stirring
30 to dilute the slurry and keep it stirrable. The diluted
 slurry was stirred for 30 minutes, filtered and the cake
 was washed with acetone. The cake was twice reslurried
 in acetone and then dried in air. The resulting dark
 red semicrystalline polyester powder, containing
35 19.95 weight percent of the anthraquinone colorant
 residue, has an inherent viscosity of 0.548, a melting
 temperature of 195°C, a weight average molecular weight

- 47 -

of 31,409, a number average molecular weight of 19,323 and a polydispersity value of 1.62. The yield was 121 g.

5 Preparation 20

The following materials were placed in a 2.0L three-necked, round-bottom flask:

- 10 540.26 g (2.785 mol) dimethyl terephthalate
405.00 g (4.50 mol) 1,4-butanediol
0.0722 g Ti from a n-butanol solution of titanium tetraisopropoxide
15 142 g (0.430 mol) methine yellow colorant [methyl 3-[4-[[[acetyloxy)ethyl]ethylamino]-2-methylphenyl]-2-cyano-2-propenoate]

20

The flask was equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents were heated in a Belmont metal bath with a
25 nitrogen sweep over the reaction mixture as the temperature was increased to 200°C and then to 230°C over 2 hours and held at 230°C for 2 additional hours. Vacuum was applied until the pressure was reduced to 0.5 mm Hg. The polycondensation was completed by
30 heating the flask for 1 hour under a pressure of 0.1 to 0.5 mm Hg while allowing the temperature to rise to 240°C. The vacuum was then relieved with nitrogen and methyl benzoate (450 mL) was added slowly and stirred to
35 solution over about 10 minutes with the flask still in the metal bath. The resulting solution was transferred to a 4 L beaker and stirred until crystallization occurred. Acetone (1.0 L) was added slowly with

- 48 -

stirring to dilute the slurry and keep it stirrable. The diluted slurry was stirred for 45 minutes, filtered and the cake was washed with acetone. The cake was twice reslurried in acetone and then dried in air. The

5 resulting dark yellow semicrystalline polyester powder, containing 19.66 weight percent of the methine colorant residue, had an inherent viscosity of 0.277, a melting temperature of 206°C, a weight average molecular weight of 15,137, a number average molecular weight of 10,835

10 and a polydispersity value of 1.39. The yield was 688 g.

EXAMPLE 1

Kodar® PETG copolyester 6763 (Eastman Kodak

15 Company) (9.85 lb of previously dried pellets) was blended with 0.15 lb of poly(1,4-butylene terephthalate) colorant composition prepared in Preparation 2. The materials were then compounded on a 1.75 in. Killion single screw extruder equipped with a mixing screw and

20 extruded at 500-550°F into a thin film having a thickness of 2-3 mils. The red colored polyester film is glossy and has good clarity and the color development is excellent. No problems of sublimation or colorant migration were observed. Kodar® PETG copolyester 6763

25 (Eastman Kodak Company) is a clear amorphous polymer with a glass transition temperature (T_g) of about 178°F (81°C) as determined by Differential Scanning Calorimetry.

30 EXAMPLE 2

Example 1 was repeated except 0.15 lb of the poly(1,4-butylene terephthalate) colorant composition of Preparation 1, which has a higher inherent viscosity

- 49 -

relative to the colorant composition used in Example 1, was used as the colorant composition. The red colored polyester film had similar color and clarity to that prepared in Example 1.

5.

EXAMPLE 3

The poly(1,4-butylene terephthalate) colorant composition of Preparation 3 (0.15 lb) was blended with Kodar® PETG copolyester 6763 (Eastman Kodak Company) (9.85 lb of previously dried pellets). The materials were compounded on a 1.75 in. Killion single screw extruder equipped with a mixing screw and extruded at about 500-550°F into a thin film having a thickness of about 2-3 mils. The film thus produced had a bright yellow color and good clarity. No problem of loss of colorant by sublimation was observed and excellent color development was achieved.

15

EXAMPLE 4

Example 3 was repeated except 0.15 lb of the poly(1,4-butylene terephthalate) colorant composition of Preparation 4, which has a higher inherent viscosity relative to the colorant composition used in Example 3, was used as the colorant composition. The quality of the film and color development were excellent and similar to that obtained in Example 3.

20

25

EXAMPLE 5

Example 1 was repeated except that the thermoplastic polyester used was Kodar® A150 copolyester (Eastman Kodak Company) (9.85 lb), which is a copolyester produced from the reaction of terephthalic acid and isophthalic acid with the glycol 1,4-

30

- 50 -

cyclohexanedimethanol and which has a glass transition temperature (T_g) at 87°C (189°F).

EXAMPLE 6

- 5 Example 2 was repeated except the thermoplastic polyester used was Kodar® A150 copolyester (Eastman Kodak Company) (9.85 lb).

EXAMPLE 7

- 10 Example 3 was repeated except the thermoplastic polyester used was Kodar® A150 copolyester (Eastman Kodak Company) (9.85 lb).

EXAMPLE 8

- 15 Example 4 was repeated except the thermoplastic polyester used was Kodar® A150 copolyester (Eastman Kodak Company) (9.85 lb).

 The quality of the films thus produced in Examples 4-8 was excellent with good clarity and color development being achieved. No problems of sublimation of colorants were observed.

20

EXAMPLE 9

- The polyester colorant composition of Preparation 2 (0.2 lb) was blended with 9.8 lb of Tenite® polypropylene P6M5U-033 copolymer (Eastman Kodak Company). The materials were compounded at about 400°F on a 30 mm corotating intermeshing twin screw extruder (Werner-Pfleiderer Corp.) and pelletized. The pellets were then extruded into film having a thickness of about 2-3 mils using a Killion single screw extruder at about 450°F. Compared to polypropylene film colored using
- 25
- 30

- 51 -

conventional inorganic and organic colorants, the red film was brighter, glossier and less hazy.

EXAMPLE 10

5 The polyester colorant composition of Preparation 1 (0.2 lb), which has a higher inherent viscosity relative to the colorant composition used in Example 9, and 9.8 lb of Tenite® polypropylene P6M5U-033 copolymer (Eastman Kodak Company) were blended and the material
10 extruded into a 2-3 mil thick film according to the procedure of Example 9 to give a red polypropylene film which was brighter, glossier and less hazy than colored polypropylene film thus prepared using conventional
15 inorganic or organic colorants.

EXAMPLE 11

 The polyester colorant composition of Preparation 3 (0.2 lb) was blended with 9.8 of Tenite® polypropylene P6M5U-033 copolymer (Eastman Kodak Company) and the
20 material extruded into a 2-3 mil thick film according to the procedure of Example 9 to give a yellow polypropylene film which was brighter, glossier and less hazy than colored polypropylene film thus prepared using
25 conventional inorganic or organic colorants.

EXAMPLE 12

 The polyester colorant composition of Preparation 4 (0.2 lb), which has a higher inherent viscosity relative to the colorant composition used in Example 11, and
30 9.8 lb of Tenite® polypropylene P6M5U-033 copolymer (Eastman Kodak Company) were blended and the materials extruded into a 2-3 mil thick film according to the

- 52 -

procedure of Example 9 to provide a yellow film of high quality.

EXAMPLE 13

5 The polyester colorant composition of Preparation 2
(0.2 lb) was blended with 9.8 lb of Tenite® poly-
propylene P4G3Z-039 homopolymer (Eastman Kodak Company)
and the materials compounded at about 400°F on a 30 mm
corotating intermeshing twin screw extruder
10 (Werner-Pfleiderer Corp.) and pelletized. The pellet
were then extruded into film having a thickness of about
2-3 mils using a Killion single screw extruder at about
400°F. High quality red colored film was produced with
good color development being achieved.

15

EXAMPLE 14

 The polyester colorant composition of Preparation 1
(0.2 lb) which has a higher inherent viscosity relative
to the colorant composition used in Example 13, and
20 9.8 lb of Tenite® polypropylene P4G3Z-039 homopolymer
(Eastman Kodak Company) were blended and converted into
2-3 mil thick film according to the procedure of
Example 13 to provide a high quality red film.

EXAMPLE 15

25 The polyester colorant composition of Preparation 3
(0.2 lb) was blended with 9.8 lb of Tenite® poly-
propylene P4G3Z-039 homopolymer (Eastman Kodak Company)
and the material extruded in 2-3 mil thick film
30 according to the procedure of Example 13 to provide a
high quality yellow film.

EXAMPLE 16

The polyester colorant composition of Preparation 4 (0.2 lb), which has a higher inherent viscosity relative to the colorant composition used in Example 15, and
5 9.8 lb of Tenite® polypropylene P4G3Z-039 homopolymer (Eastman Kodak Company) were blended and the materials extruded into a 2-3 mil thick film according to the procedure of Example 13 to give a yellow film of high quality.

10

EXAMPLE 17

Makrolon 2608 polycarbonate (Mobay) (410.68 g of material ground to particle size of about 3 mm) and
9.32 g of the colorant composition of Preparation 10
15 were dry blended and the blend dried at 110°C for 16 hours in a vacuum oven. After drying, the material was melt blended and extruded at about 305°C into 12-13 mil film on a C. W. Brabender 3/4 inch extruder (25 to 1 L/D). The film had excellent clarity and was cyan in
20 color.

EXAMPLE 18

Makrolon 2608 polycarbonate (Mobay) (417.29 g of material ground to particle size of about 3 mm) and
25 2.71 g of methine yellow colorant composition of Preparation 5 were blended and converted into a 12-13 mil film according to the procedure in Example 17. The bright yellow film thus produced had good clarity and excellent fastness when exposed to light.

30

EXAMPLE 19

Makrolon 2608 polycarbonate (Mobay) (417.20 g of material ground to particle size of about 3 mm) and

- 54 -

2.80 g of anthraquinone red colorant composition of Preparation 6 were blended and converted into a 12-13 mil film according to the procedure of Example 17. Excellent clarity and good color development were obtained and the red colored had excellent light-fastness.

EXAMPLE 20

10 Makrolon 2608 polycarbonate (Mobay) (416.77 g of material ground to particle size of about 3 mm) and 3.23 g of the blue anthraquinone colorant composition of Preparation 12 were blended and converted into a 12-13 mil film according to the procedure of Example 17. The bright blue film thus produced had excellent clarity.

15

EXAMPLE 21

Makrolon 2608 polycarbonate (Mobay) (417.29 g of material ground to particle size of about 3 mm) and 2.71 g of the yellow anthraquinone colorant composition of Preparation 11 were blended and extruded into a 12-13 mil film according to the procedure of Example 17. The film had a neutral yellow color and had excellent fast-ness to light.

25

EXAMPLE 22

Makrolon 2608 polycarbonate (Mobay) (411.60 g of material ground to particle size of about 3 mm) and 8.40 g of red anthraquinone colorant composition of Preparation 7 were blended and converted into a 12-13 mil film exactly as described in Example 17. The bright red film thus produced had excellent clarity and good development of color.

30

- 55 -

EXAMPLE 23

5 Makrolon 2608 polycarbonate (Mobay) (414.75 g of material ground to particle size of about 3 mm) and 5.25 g of the colorant composition of Preparation 8 were blended and converted into a 12-13 mil film as described in Example 17. A bright magenta colored film having good clarity and fastness to light was thus produced.

EXAMPLE 24

10 Makrolon 2608 polycarbonate (Mobay) (411.60 g of material ground to particle size of about 3 mm) and 8.40 g of red methine colorant composition of Preparation 13 were blended and converted into a 12-13 mil film according to the procedure of Example 17. The
15 film thus produced had good clarity and is bright red in color.

EXAMPLE 25

20 Makrolon 2608 polycarbonate (Mobay) (411.60 g of material ground to particle size of about 3 mm) and 8.40 g of anthraquinone blue colorant composition of Preparation 9 were blended and converted into a 12-13 mil film according to the procedure in Example 17. The film thus produced had a neutral blue color and had good
25 clarity.

EXAMPLE 26

30 A 1:1 blend of Kodar® PCT 3879 polyester (Eastman Kodak Company) and Makrolon 2608 polycarbonate (Mobay), along with 5 wt % of an acrylic impact modifier, was melt blended on a Werner & Pfleiderer ZSK-28 twin screw extruder. This composition also contained 0.125 wt % of the colorant composition of Preparation 15, 0.025 wt %

- 56 -

of the colorant composition of Preparation 17, 0.150 wt % of the colorant composition of Preparation 18 and 0.050 wt % of TiO_2 . After compounding, this material was molded on a New Britain 175 injection molding machine into double-gated 0.125-inch thick plaques. Surprisingly, the region surrounding the weld line on these plaques was virtually indistinguishable from the rest of the plaque.

10 EXAMPLE 27

A composition similar to that in Example 26 was created, but the colorant system composition was changed to 0.125 wt % of the composition of Preparation 16, 0.150 wt % of the composition of Preparation 19, 0.025 wt % of the composition of Preparation 20 and 0.050 wt % TiO_2 . This material was compounded and molded as described in Example 26. Again, the region surrounding the weld line in the molded plaques was unexpectedly indistinguishable from the remainder of the part.

20

EXAMPLE 28

The colorant system used in Example 27 was dispersed in Makrolon 2608 polycarbonate (Mobay). This material was compounded and molded as described in Example 26. Again, the region surrounding the weld line in the molded plaques was unexpectedly indistinguishable from the remainder of the part.

25 COMPARATIVE EXAMPLE 1

30 A composition similar to that in Example 26 was created, except that the colorant system was replaced by a typical pigment system consisting of Chromalox 4870 (G-22 pigment), Mapico Red 297 (R-33 pigment),

- 57 -

Cadmium Yellow (Y-74 pigment), and TiO_2 . This material was compounded and molded as described in Example 26. In this case, a dark, discolored streak was observed along the weld line in the molded plaque, demonstrating the unobviousness of the nearly invisible weld line observed in Examples 26 and 27.

- 58 -

CLAIMS

1. A colored thermoplastic polymer blend, which
comprises one or more thermoplastic polymers having
5 blended therein one or more colored polyesters,
said colored polyesters having copolymerized
therein from about 1 weight percent to about
50 weight percent of one or more thermally-stable
difunctional colorant residues.
10
2. The colored thermoplastic polymer blend of Claim 1
wherein the thermally-stable colorant residue is
present in the colored polyester in a
concentration of about 5 weight percent to
15 30 weight percent.
3. The colored thermoplastic polymer blend of Claim 1,
wherein the thermoplastic polymer is selected from
a list consisting of polyesters, polyolefins,
20 polyamides, polyimides, polyvinyl chloride,
polyvinylidene chloride, polyurethanes, poly-
carbonates, cellulose esters, polyacrylates,
polyvinylesters, polyester-amides, polystyrene,
acrylonitrile-butadiene-styrene, and styrene-
25 acrylonitrile.
4. The colored thermoplastic polymer blend of Claim 1,
wherein the thermoplastic polymer is a polyolefin.
- 30 5. The colored thermoplastic polymer blend of Claim 4,
wherein the polyolefin is polyethylene, poly-
propylene, or polybutylene.

- 59 -

6. The colored thermoplastic polymer blend of Claim 4, wherein the polyolefin is a copolymer comprising any combination of polyethylene, polypropylene, or polybutylene.
- 5 7. The colored thermoplastic polymer blend of Claim 1, wherein at least one of the thermoplastic polymers is a polyamide.
- 10 8. The colored thermoplastic polymer blend of Claim 1, wherein at least one of the thermoplastic polymers is a polyurethane.
- 15 9. The colored thermoplastic polymer blend of Claim 1, wherein at least one of the thermoplastic polymers is polyvinyl chloride.
- 20 10. The colored thermoplastic polymer blend of Claim 1, wherein at least one of the thermoplastic polymers is polyvinylidene chloride.
- 25 11. The colored thermoplastic polymer blend of Claim 1, wherein at least one of the thermoplastic polymers is a polycarbonate.
12. The colored thermoplastic polymer blend of Claim 1, wherein at least one of the thermoplastic polymers is a polyester.
- 30 13. The colored thermoplastic polymer blend of Claim 1, wherein at least one of the thermoplastic polymers is a cellulose ester, or mixtures thereof.

- 60 -

14. The colored thermoplastic polymer blend of Claim 13, wherein at least one of the thermoplastic polymers is selected from a list consisting of cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate propionate, and cellulose acetate butyrate.
15. The colored thermoplastic polymer blend of Claim 1, wherein at least one of the thermoplastic polymers is a polyacrylate.
16. The colored thermoplastic polymer blend of Claim 1 wherein at least one of the thermoplastic polymers is a polyester-amide.
17. The colored thermoplastic polymer blend of Claim 1 wherein at least one of the thermoplastic polymers is polystyrene.
18. The colored thermoplastic polymer blend of Claim 1 wherein the thermoplastic polymer is a blend of a polyester and a polycarbonate.
19. A shaped or formed article comprised of the colored thermoplastic polymer blend of Claim 1.
20. A shaped or formed article comprised of the colored thermoplastic polymer blend of Claim 2.
21. A shaped or formed article comprised of the colored thermoplastic polymer blend of Claim 3.

- 61 -

22. A shaped or formed article comprised of the colored thermoplastic polymer blend of Claim 5.
23. A shaped or formed article comprised of the colored thermoplastic polymer blend of Claim 18.
24. The colored thermoplastic polymer blend of Claim 1 wherein said colored polyester is a colored poly-(1,4-butylene terephthalate).
25. The colored thermoplastic polymer blend of Claim 1 wherein said colored polyester is a colored poly-(1,4-butylene terephthalate) having about 5 weight percent to 30 weight percent of one or more thermally-stable colorant residues copolymerized therein.
26. The colored thermoplastic polymer blend of Claim 1 wherein said colored polyester is a colored poly-(1,4-butylene terephthalate) which has been modified by dissolution-crystallization-precipitation to impart crystallizing thereto and has copolymerized therein at least 5.0 weight percent, based on the weight of the colored polyester, the residue of one or more thermally stable difunctional colorants.

INTERNATIONAL SEARCH REPORT

PCT/US 92/01003

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08L101/00; //(C08L101/00,67:02)C08L67/02

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System

Classification Symbols

Int.Cl. 5

C08L

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are included in the Fields Searched⁸III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
P,X	EP,A,0 417 017 (EASTMAN KODAK COMP.) 13 March 1991 see page 2, line 1 - line 48 see page 3, line 25 - line 27 see page 9, line 3 - line 16 see page 10, line 9 - line 20 ---	1-26
P,X	WO,A,9 110 693 (EASTMAN KODAK COMP.) 25 July 1991 see page 1, line 1 - line 14 see page 2, line 4 - line 9 see page 4, line 11 - page 5, line 1 see page 38, line 1 - page 39, line 23 see page 41, line 30 - page 42, line 13 ---	1-26
X	GB,A,1 225 566 (RHODIACETA) 17 March 1971 cited in the application see page 1, line 78 - line 84 see page 2, line 65 - line 106; claims 1,8-12 ---	1,19,24
	--- -/-	

^{*} Special categories of cited documents: ¹⁰

- ^{"A"} document defining the general state of the art which is not considered to be of particular relevance
- ^{"E"} earlier document but published on or after the international filing date
- ^{"L"} document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- ^{"O"} document referring to an oral disclosure, use, exhibition or other means
- ^{"P"} document published prior to the international filing date but later than the priority date claimed

^{"T"} later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention^{"X"} document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step^{"Y"} document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art^{"&"} document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

15 JUNE 1992

Date of Mailing of this International Search Report

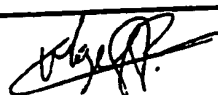
23.06.92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

MAZET J.



III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	<p>US,A,4 116 923 (GATTNER ET AL.) 26 September 1978 cited in the application see abstract see column 1, line 14 - line 45 see column 2, line 41 - line 55; claims</p>	1-4, 19-21
Y	<p>US,A,4 359 570 (T.G. DAVIS ET AL.) 16 November 1982 cited in the application see column 1, line 11 - line 18 see column 2, line 31 - line 45 see column 3, line 17 - column 4, line 45 see column 9, line 4 - line 58 see column 10, line 53 - column 11, line 9</p>	1-25
Y	<p>US,A,4 477 635 (MITRA) 16 October 1984 cited in the application see column 4, line 12 - line 16 see column 10, line 18 - line 31 see examples 22-24</p>	1-25
A	<p>EP,A,0 215 322 (MILLIKEN RESEARCH CORPORATION) 25 March 1987 see column 1, line 7 - line 12 see column 1, line 30 - line 50 see column 2, line 31 - column 3, line 9; claims</p>	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9201003
SA 57660**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 15/06/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0417017	13-03-91	US-A- 5032670	16-07-91
		EP-A- 0485520	20-05-92
		WO-A- 9103508	21-03-91
WO-A-9110693	25-07-91	US-A- 5106942	21-04-92
		EP-A- 0462262	27-12-91
GB-A-1225566	17-03-71	CH-A- 496061	15-09-70
		DE-A- 1916169	03-09-70
		FR-A- 1570579	13-06-69
		NL-A- 6904410	01-10-69
US-A-4116923	26-09-78	DE-A- 2613493	06-10-77
		BE-A- 853035	30-09-77
		FR-A- 2346385	28-10-77
		GB-A- 1566043	30-04-80
		JP-A- 52117996	03-10-77
		NL-A- 7703258	04-10-77
US-A-4359570	16-11-82	EP-A- 0040139	18-11-81
		JP-A- 57003851	09-01-82
US-A-4477635	16-10-84	None	
EP-A-0215322	25-03-87	US-A- 4640690	03-02-87
		AU-B- 582461	23-03-89
		AU-A- 6175286	19-03-87
		JP-B- 3040154	18-06-91
		JP-A- 62104875	15-05-87
		US-A- 4812141	14-03-89
		US-A- 4732570	22-03-88